

WATER TRANSPORT ACROSS CATION-EXCHANGE MEMBRANES. III.
MODEL FOR THE INTERPRETATION OF THE INFLUENCE OF
POLARIZATION LAYERS ON THE WATER TRANSPORT NUMBERS

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(NASA-TT-F-16168) WATER TRANSPORT ACROSS
CATION-EXCHANGE MEMBRANES. 3: MODEL FOR
THE INTERPRETATION OF THE INFLUENCE OF
POLARIZATION LAYERS ON THE WATER TRANSPORT
NUMBERS (Kanner (Leo) Associates) 30 p HC G3/85 14618
N75-20162
Unclas

Translation of "Transport d'eau dans les membranes échangeuses
de cations. III. Modèle pour l'interprétation de l'influence
des couches de polarisation sur les nombres de transport
d'eau," Journal de Chimie Physique, Vol. 71, No. 6,
1974, pp. 828-835



STANDARD TITLE PAGE

1. Report No. NASA TT F-16168	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle WATER TRANSPORT ACROSS CATION-EXCHANGE MEMBRANES. III. MODEL FOR THE INTERPRETATION OF THE INFLUENCE OF POLARIZATION LAYERS ON THE WATER TRANSPORT NUMBER		5. Report Date March 1975	
		6. Performing Organization Code	
7. Author(s) C. Ripoll, M. Demarty and E. Selegny, Laboratory of Macromolecular Chemistry, Faculty of Science and Technique at Rouen		8. Performing Organization Report No.	
		10. Work Unit No.	
9. Performing Organization Name and Address Leo Kanner Associates Redwood City, California 94063		11. Contract or Grant No. NASw-2481	
		13. Type of Report and Period Covered Translation	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration, Washington, D.C. 20546		14. Sponsoring Agency Code	
15. Supplementary Notes Translation of "Transport d'eau dans les membranes échangeuses de cations. III. Modèle pour l'interprétation de l'influence des couches de polarisation sur les nombres de transport d'eau," Journal de Chimie Physique, Vol. 71, No. 6, 1974, pp. 828-835			
16. Abstract A theoretical interpretation of electroosmotic measurements of a cation-exchange membrane under natural or imposed convection is discussed. The calculations are based on the steady-state flow properties described by Nernst-Planck equations. The membrane is assumed to be homogeneous, and the thickness of the polarization layers, described in Nernst's hypothesis, is supposed to be identical. It was possible to express the parameters which influence the electroosmotic flow, especially the influence of concentration polarization. It is shown that polarization is one of the factors that make it possible to explain the dependence of the water transport number on the current and that this dependence is closely connected with the types of convection that exist on the membrane/solution interfaces.			
17. Key Words (Selected by Author(s))		18. Distribution Statement Unclassified-Unlimited	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 25	22. Price

List of Symbols

a	Numerical coefficient, equation (28)
a_s	Activity of the salt
g	Acceleration due to gravity
h	Height of the membrane
l	Thickness of the membrane
t_i	Transport number of an ion in the system defined by (5)
t_i^0	Transport number of an ion in solution
$t_0(\text{app})$	Apparent water transport number
t_{0b}	Barycentric water transport number
t_{0s}	Water transport number defined by (18)
U_b	Barycentric speed
A_1, A_2	Constants
\bar{C}_i	Molarity of an ion in the membrane (interstitial solution)
$\bar{C}_i(e)$	Molarity of an ion in the membrane at equilibrium
$C(I), C(II)$	Interfacial concentrations defined by Fig. 1
$\bar{C}(I), \bar{C}(II)$	Interfacial concentrations defined by Fig. 1
$C^0(I), C^0(II)$	Concentration of the solutions defined by Fig. 1
ΔC	Concentration difference in a Nernst film, Fig. 1
\bar{D}_i	Diffusion coefficient of an ion in the membrane
$\bar{D}_i(e)$	Diffusion coefficient of an ion in the membrane at equilibrium
\bar{D}_i^*	Diffusion coefficient of an ion defined by (15) and (16)
D_s^*	Diffusion coefficient of salt defined by (17)
$D_{\bar{s}}$	Diffusion coefficient of salt in simple solution

F	Faraday
I	Current density
$(J_i)_b$	Flow of the i species with regard to the center of the masses
$(J_i)_c$	Flow of the i species with regard to the cell
$(J_v)_c$	Voluminal flow with regard to the cell
K_E, K_D	Proportionality coefficients between I and $\Delta C^{5/4}$ under natural convection in profiles (a) and (b), Fig. 2
M_i	Molar mass of the i species
N	Avogadro's number
P	Pressure
R	Ideal gas constant
T	Absolute temperature
\bar{V}_i	Partial molar volume of the i species
X	Membrane capacity
α	Density coefficient of the electrolyte
γ	Activity coefficient in the molar scale
δ	Thickness of the Nernst layer
δ_0	Thickness of the hydrodynamic layer
\bar{n}_i	Electrochemical potential of the i species
\bar{n}_i	Electrochemical potential of the i species in the membrane
μ_i	Chemical potential of the i species
ν	Kinematic viscosity
σ	Relation of the diffusion coefficient defined by (16)
$\sigma(e)$	Relation of the diffusion coefficients at equilibrium

Φ	Voluminal fraction of the solution in the membrane
ϕ	Electric potential
0, 1, 2	Indices corresponding to water, cation, and anion, respectively

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Introduction

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In a previous publication [1], we presented the experimental results of the measurements of water transport numbers obtained with different concentration profiles on the membrane/solution interfaces. Our task here is to develop a model which makes it possible for us to explain the phenomena we observed.

There are several theories of electroosmosis; we can roughly classify them into three categories:

a) the simplified theories which consider water to be transported by ions in the form of hydration water [2, 3, 4];

b) theories based on the principles of the thermodynamics of irreversible processes; they cause an intervention of the coefficients of interaction between different species present in the membrane [5, 6, 7];

c) the thermodynamic theories which calculate the voluminal flow from Nernst-Planck equations; the barycentric speed which intervenes in these equations is obtained by resolution of the Navier-Stokes equation, generally with the aid of a capillary model for the membrane [8, 9, 10].

* Numbers in the margin indicate pagination in the foreign text.

Let us further mention Manning's calculation with the aid of a model of a network of discrete charges [11].

None of these theories was developed for the purpose of explaining the dependence of the water transport number on current density, which has been observed by many researchers [12, 13, 14]; they all assume that the polarization is negligible, and do not take into consideration the type of convection on the membrane/solution interfaces; with a simple theoretical interpretation, we will show that exactly these factors condition the electroosmotic flow. We will see that even if it is small, the concentration polarization cannot be ignored.

II. Theory

The isothermal and isobaric system we studied is made up of a cation-exchange membrane which separates the solution of a 1-1 electrolyte (Fig. 1).

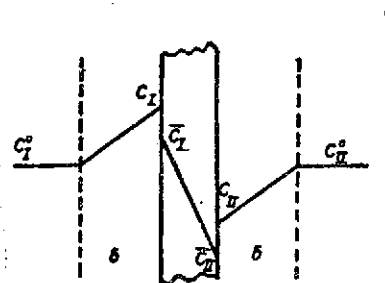


Fig. 1. General sketch of the concentration profile of salt in the system studied.

The polarization films formed at the time of the passage of the current are described in the Nernst hypothesis. In the following calculation we will assimilate the membrane in two phases¹; we will assume that there is no coupling between the flows which will be described by Nernst-Planck equations. In the following, the system will always be considered to be in a stationary state.

The voluminal flow is defined by:

$$(J_v)_c = (J_1)_c \bar{V}_1 + (J_2)_c \bar{V}_2 + (J_0)_c \bar{V}_0 \quad (1)$$

¹ Phase of interstitial solution and membrane phase formed by the matrix.

In this relation, indices 1, 2, and 0 characterize the compensating ion, the co-ion and the solvent, respectively. \bar{V}_i is the partial molar volume of the different species of the membrane (considered in the following to be independent of the concentration and equal to the values in solution) and $(J_i)_c$ is flow with regard to the cell.

If U_b represents the barycentric speed and $(J_i)_b$ the flow with regard to the center of the masses, we have

$$(J_i)_c = (J_i)_b + \bar{C}_i U_b \quad (2)$$

\bar{C}_i is the molarity in the inflating solution.

This equations offers a correct description of the flows in a homogeneous macroscopic medium. Certain researchers [19, 25] have suggested that a correction be introduced into the convective term in order to explain the interactions on the microscopic scale. We do not introduce this correction here; our task is to develop a macroscopic model and to test its application limit.

When we take into consideration the conservation of mass relation (3):

$$M_1(J_1)_b + M_2(J_2)_b + M_0(J_0)_b = 0 \quad (3)$$

in which M_i represents the molar mass, and relations (1) and (2), we find:

$$\begin{aligned} \frac{F(J_0)_c}{iV_0} = & \left(\frac{\bar{V}_1}{V_0} - \frac{M_1}{M_0} \right) i_1 - \left(\frac{\bar{V}_2}{V_0} - \frac{M_2}{M_0} \right) \\ & + U_b \frac{F}{V_0 i M_0} (\bar{C}_0 M_0 + \bar{C}_1 M_1 + \bar{C}_2 M_2) \end{aligned} \quad (4)$$

In this expression one uses the definitions $\bar{V}_s = \bar{V}_1 + \bar{V}_2 =$ partial molar volume of salt.

$$t_1 = \frac{F(J_1)_c}{I} = \text{real transport number of the counter-ion in the system} \quad (5)$$

The dimensionless quantity thus obtained is generally called the apparent water transport number; we will write

$$t_{o(opp)} = \frac{F(J_1)_c}{IV_0} \quad (6)$$

In the following, \bar{V}_0 will be taken as equal to 18 cm³/mole even in the membrane, which is a good approximation (15).

By analogy, we write

$$t_{ob} = \frac{FU_b}{V_0 I} \quad (7)$$

The dimensionless quantity

$$\frac{\bar{V}_0}{M_0} (\bar{C}_0 M_0 + \bar{C}_1 M_1 + \bar{C}_2 M_2)$$

is numerically equal to the voluminal mass of the inflating solution; as a first approximation, we will take 1.

Then the expression

$$t_{ob} = \left(\frac{\bar{V}_1}{\bar{V}_0} - \frac{M_1}{M_0} \right) \times t_1 - \left(\frac{\bar{V}_2}{\bar{V}_0} - \frac{M_2}{M_0} \right) \quad (8)$$

represents the water transport number which could be observed at zero barycentric speed.

Finally, relation (4) will be written with our notations:

$$t_0(\text{app}) = t_{0s} + t_{0b} \quad (9)$$

In a first stage, we will relate t_{0b} to t_1 and the difference in chemical potential of the salt occurring on the interfaces of the membrane. Flows $(J_i)_b$ will be expressed by the Nernst-Planck unidimensional equation:

$$(J_i)_b = -\frac{\bar{D}_i \bar{C}_i}{RT} \frac{d\bar{\eta}_i}{dx} \quad (10)$$

in which \bar{D}_i represents the effective diffusion coefficient of the i species in the membrane; it combines all the electrostatic interactions and the contour factor. We will generally consider it to be dependent on the concentration. $\bar{\eta}_i$ is the electrochemical potential of the i species in the membrane, defined by the well-known relation:

$$\bar{\eta}_i = \bar{\mu}_i + Z_i \bar{\phi} + \bar{V}_i P$$

in which $\bar{\mu}_i$ is the chemical potential, $\bar{\phi}$ is the electric potential, P is the pressure, and Z_i is the algebraic value of the ion charge.

Thus, for a 1/1 electrolyte we can write:

$$\left. \begin{aligned} \frac{F(J_1)_e}{IV_0} = \frac{t_1}{V_0} &= -\frac{F}{V_0 I} \cdot \frac{\bar{D}_1 \bar{C}_1}{RT} \cdot \frac{d\bar{\eta}_1}{dx} + \bar{C}_1 t_{0b} \\ -\frac{F(J_2)_e}{IV_0} = \frac{t_2}{V_0} &= \frac{F}{V_0 I} \cdot \frac{\bar{D}_2 \bar{C}_2}{RT} \cdot \frac{d\bar{\eta}_2}{dx} - \bar{C}_2 t_{0b} \end{aligned} \right\} \quad (11)$$

In the stationary state, t_1 and t_2 are constant. On the other hand, U_b , barycentric speed defined by

$$U_b = \frac{\sum M_i(U)_e}{\sum \bar{C}_i M_i}$$

is a function of position in the membrane. However, in the case of an ion-exchange membrane in the presence of dilute solutions, the denominator of the above expression varies little; since the numerator is constant in the stationary state, we will concede that U_b is a constant independent of position in the membrane. Let us remember that this approximation will be the more justified, the smaller the concentration gradients are in the membrane.

We integrate equations (11) on the entire thickness l in the membrane:

$$\left. \begin{aligned} t_1 \frac{l}{\bar{V}_a} &= -\frac{F}{\bar{V}_a IRT} \int_{0+}^L \bar{D}_1 \bar{C}_1 \frac{d\bar{\eta}_1}{dx} dx + t_{00} \langle \bar{C}_1 \rangle l \\ t_2 \frac{l}{\bar{V}_s} &= \frac{F}{\bar{V}_s IRT} \int_{0+}^L \bar{D}_2 \bar{C}_2 \frac{d\bar{\eta}_2}{dx} dx - t_{00} \langle \bar{C}_2 \rangle l \\ \langle \bar{C}_i \rangle &= \frac{1}{l} \int_{0+}^L \bar{C}_i(x) dx \end{aligned} \right\} \quad (12)$$

By using the formula of the average, we can further write:

$$\left. \begin{aligned} \int_{0+}^L \bar{D}_1 \bar{C}_1 \frac{d\bar{\eta}_1}{dx} dx &= \bar{D}_1(\lambda) \bar{C}_1(\lambda) \Delta \bar{\eta}_1 \quad \lambda \in (0, l) \\ \int_{0+}^L \bar{D}_2 \bar{C}_2 \frac{d\bar{\eta}_2}{dx} dx &= \bar{D}_2(\mu) \bar{C}_2(\mu) \Delta \bar{\eta}_2 \quad \mu \in (0, l) \end{aligned} \right\} \quad (13)$$

with

$$\Delta \bar{\eta}_i = \int_{0+}^L d\bar{\eta}_i$$

If we take into consideration the continuity of the electrochemical potentials on the interfaces

$$\Delta \bar{\eta}_i = \Delta \eta_i$$

and

$$\Delta \eta_1 + \Delta \eta_2 = \Delta \mu_s$$

which is the difference of the chemical potential of the salt on the interfaces for an isobaric system; by combining equations (12), we obtain:

$$t_{0b} \times \left[\frac{\langle \bar{C}_1 \rangle}{\bar{D}_1(\lambda) \bar{C}_1(\lambda)} + \frac{\langle \bar{C}_2 \rangle}{\bar{D}_2(\mu) \bar{C}_2(\mu)} \right] = \frac{1}{V_0} \left(\frac{t_1}{\bar{D}_1(\lambda) \bar{C}_1(\lambda)} - \frac{t_2}{\bar{D}_2(\mu) \bar{C}_2(\mu)} \right) + \frac{F}{V_0 I R T} \Delta \mu_s \quad (14)$$

With the following definitions:

$$\bar{D}_1^* = \bar{D}_1(\lambda) \frac{\bar{C}_1(\lambda)}{\langle \bar{C}_1 \rangle} \quad (15)$$

$$\bar{D}_2^* = \bar{D}_2(\mu) \frac{\bar{C}_2(\mu)}{\langle \bar{C}_2 \rangle} \quad (16)$$

$$\bar{D}_i^* = \frac{\bar{D}_1^* \bar{D}_2^*}{\bar{D}_1^* + \bar{D}_2^*} \quad (17)$$

$$\sigma = \frac{\bar{D}_1^*}{\bar{D}_2^*} \quad (18)$$

Taking into consideration:

$$\Delta \mu_s = R T \ln \frac{a_s(II)}{a_s(I)} \quad (19)$$

in which $a_s(II)$ and $a_s(I)$ are the activities of the salt in the solution on the membrane/compartment I and membrane/compartment II interfaces, respectively, we finally obtain:

$$t_{0b} = \frac{\bar{D}_2^*}{V_0} \left(\frac{t_1}{\bar{D}_1^* \langle \bar{C}_1 \rangle} - \frac{t_2}{\bar{D}_2^* \langle \bar{C}_2 \rangle} \right) + \frac{F \bar{D}_2^*}{V_0 I} \ln \frac{a_s(II)}{a_s(I)} \quad (20)$$

or, by using definition (18):

$$t_{0b} = \frac{1}{(1+\sigma)V_0} \left(\frac{t_1}{\langle \bar{C}_1 \rangle} - \frac{t_2 \sigma}{\langle \bar{C}_2 \rangle} \right) + \frac{\sigma \bar{D}_2^*}{(1+\sigma)V_0} \cdot \frac{F}{I} \ln \frac{a_s(II)}{a_s(I)} \quad (21)$$

Expression (20) or (21) constitutes a relation between t_{0b} and t_1 . In order to go further, let us use the constancy of the $(J_1)_c$ flows in the stationary state.

The counter-ion flow in a Nernst film can be written:

$$\frac{t_1 I}{F} = (J_1)_c = t_1^0(I) \frac{F}{I} + D_s(I) \frac{\Delta C}{\delta} + C(I)(J_1)_c$$

In this expression, t_1^0 is the transport number of the cation in solution, D_s is the diffusion coefficient of the electrolyte, δ is the thickness of the Nernst layer, and ΔC is the concentration difference in the Nernst film.

On interface II we have

$$\frac{t_1 I}{F} = (J_1)_c = t_1^0(II) \frac{I}{F} + D_s(II) \frac{\Delta C}{\delta} + C(II)(J_1)_c$$

Or, by taking the arithmetic mean and taking into account the preceding definitions:

$$t_1 = \frac{t_1^0(I) + t_1^0(II)}{2} + \frac{D_s(I) + D_s(II)}{2} \cdot \frac{\Delta C}{I\delta} + \bar{V}_0 \frac{C(I) + C(II)}{2} t_{0 \text{ (app)}}$$

If $C = [C(I) + C(II)]/2$, we will concede that the average values of the diffusion coefficients and the transport numbers of the preceding equations are equal to the values of D_s and t_1^0 for the electrolyte considered at concentration C .

Consequently, we can write:

$$t_1 = t_1^0 + D_s \frac{\Delta C}{I\delta} + \bar{V}_0 C t_{0 \text{ (app)}} \quad (22)$$

If we bring expression (22) into (21) and take (9) into account, we finally obtain:

$$\rho t_{0 \text{ (app)}} = t_{0s} + \frac{1}{(1+\sigma)\bar{V}_0} \left[\frac{t_1^0}{\langle \bar{C}_1 \rangle} - \frac{t_2^0 \sigma}{\langle \bar{C}_2 \rangle} + FD_s \left(\frac{1}{\langle \bar{C}_1 \rangle} + \frac{\sigma}{\langle \bar{C}_2 \rangle} \right) \frac{\Delta C}{18} \right] + \frac{\sigma \bar{D}_1^*}{(1+\sigma)\bar{V}_0} \frac{F}{H} \ln \frac{a_2(\text{II})}{a_1(\text{I})} \quad (23)$$

with

$$\rho = 1 - \frac{C}{1+\sigma} \left(\frac{1}{\langle \bar{C}_1 \rangle} + \frac{\sigma}{\langle \bar{C}_2 \rangle} \right)$$

In order to simplify the discussion of this result, we will write:

$$G(\text{I}) = \frac{\sigma \bar{D}_1^*}{\rho(1+\sigma)\bar{V}_0} \frac{F}{H} \ln \frac{a_2(\text{II})}{a_1(\text{I})} \quad (24)$$

This term represents the influence of the chemical potential difference on the interfaces of the membrane on the water transport number.

$$E(\text{I}) = \frac{1}{\rho(1+\sigma)\bar{V}_0} \left[\frac{t_1^0}{\langle \bar{C}_1 \rangle} - \frac{t_2^0 \sigma}{\langle \bar{C}_2 \rangle} + FD_s \left(\frac{1}{\langle \bar{C}_1 \rangle} + \frac{\sigma}{\langle \bar{C}_2 \rangle} \right) \frac{\Delta C}{18} \right] \quad (25)$$

Equation (23) then becomes

$$t_{0 \text{ (app)}} = \frac{t_{0s}}{\rho} + E(\text{I}) + G(\text{I}) \quad (26)$$

Before discussing the consequences of these calculations and comparing them with the experiment, we may make two comments:

1) If we consider a membrane separating two solutions of an electrolyte of the same molarity, and if we assume that there

is neither polarization nor convection in the membrane ($U_b = 0$), then

$$\begin{aligned} \langle \bar{C}_1 \rangle = \bar{C}_1(\omega) &= \text{molarity of the counter-ion in the membrane at equilibrium} \\ \langle \bar{C}_2 \rangle = \bar{C}_2(\omega) &= \text{molarity of the co-ion in the membrane at equilibrium} \\ \sigma = \sigma_e = \frac{\bar{D}_1(\omega)}{\bar{D}_2(\omega)} &= \text{relation of the diffusion coefficients at equilibrium.} \end{aligned}$$

Under these conditions, formula (20) is reduced to

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$$t_1 = \frac{\bar{D}_1(\omega) \bar{C}_1(\omega)}{\bar{D}_1(\omega) \bar{C}_1(\omega) + \bar{C}_2(\omega) \bar{C}_2(\omega)} = \bar{t}_{1(\text{app})}$$

which is the expression of the transport number of the counter-ion in the simplest case. This transport number is generally called the apparent transport number.

2) If we now acknowledge the convection in the membrane, formula (20) is reduced to:

$$t_1 = \bar{t}_{1(\text{app})} + V_0' t_{0S} X \left(\bar{t}_{1(\text{app})} + \frac{\bar{C}_2(\omega)}{X} \right)$$

$\bar{C}_1(e) - \bar{C}_2(e) = X$ is the capacity of the membrane. Or, taking (7) into account and ignoring t_{0S} , which is generally small:

$$t_1 \simeq \bar{t}_{1(\text{app})} + \frac{V_0}{\Phi} t_{0(\text{app})} X \left(\bar{t}_{1(\text{app})} + \frac{\bar{C}_2(\omega)}{X} \right)$$

This is the formula already given by Oda and Yawataya [2]. Φ has been introduced to express concentrations S and $\bar{C}_2(e)$ by a unit of volume of the inflated exchanger and not in the inflating solution; then Φ is the voluminal fraction of the solution in the inflated exchanger.

Let us now proceed to a discussion of the results and a comparison with the experiment.

III. Discussion and Comparison with Experiment

According to formulas (23) or (26), it is clear that the apparent water transport number is influenced by polarization. We can say approximately that this influence is conditioned by relation $\Delta C/I$, as we will show; we know that this relation is strongly dependent on the convection conditions on the membrane/solution interface. This is the reason why we will successively distinguish the case of natural convection and the case of imposed convection. Finally, we will discuss the case of a particular experimental arrangement.

1) Case of Natural Convection

It has been shown previously (1) that under natural convection it was possible to realize both experimental arrangements, sketched in Fig. 2. Profile (a) is called profile EQUI and profile (b) corresponds with the equiconcentration of the solutions of compartments I and II.

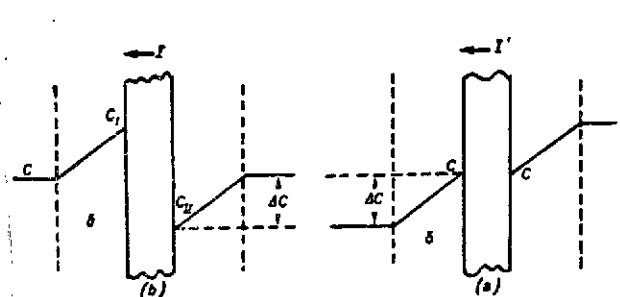


Fig. 2. Sketch of the experimental profiles. a) Interfacial equiconcentration profile; b) equiconcentration profile of the solutions.

Let us first examine the case of profile (a). Under these conditions $a_s(I) = a_s(II)$, and therefore $G(I) = 0$.

Further:

$$\left. \begin{aligned} \langle \bar{C}_1 \rangle &= \bar{C}_1(\omega) \\ \langle \bar{C}_2 \rangle &= \bar{C}_2(\omega) \\ \sigma &= \sigma_s \end{aligned} \right|$$

Formula (23) is then reduced to

$$i_{0(\text{app})} = \frac{i_{02}}{\rho} + \frac{1}{\rho(1 + \sigma_2)V_0} \left[\frac{i_1^0}{\bar{C}_1(\omega)} - \frac{i_2^0\sigma_2}{\bar{C}_2(\omega)} + FD_s \left(\frac{1}{\bar{C}_1(\omega)} + \frac{\sigma_2}{\bar{C}_2(\omega)} \right) \frac{\Delta C}{I\delta} \right] \quad (27)$$

Through an exclusively hydrodynamic approach, it has been possible to show (16) that:

$$\delta = \frac{1}{a} \left(\frac{h\nu D_s}{g\alpha} \right)^{1/4} \cdot \Delta C^{-1/4} \quad (28)$$

In this expression

h = height of the membrane

v = kinematic viscosity of the solvent

g = acceleration due to gravity

α = density coefficient of the electrolyte

a = numerical coefficient varying from 0.510 to 0.670 according to the case.

In formula (28), the quantity $D_s(F\Delta C/I\delta)$ can be written:

$$\frac{D_s F \Delta C}{I\delta} = a D_s^{3/4} \left(\frac{g\alpha}{h\nu} \right)^{1/4} F \cdot \frac{\Delta C^{5/4}}{I} \quad (29)$$

It has been shown [1] that in the case of natural convection we have:

$$I = K \Delta C^{5/4} \quad (30)$$

Coefficient K, dependent on the membrane and the system studied, is independent of I. Let K_E be the coefficient in the case of profile (a).

Let us return to equation (29); it becomes

$$\frac{\rho_s F \Delta C}{18} = \frac{a F D_s^{3/4}}{K_E(a)} \left(\frac{g \alpha}{h \nu} \right)^{1/4}$$

This quantity is independent of I . In conclusion, formula (27) shows that in the particular case of this profile the water transport number must be independent of current density. Formula (27) remains to be tested quantitatively. We will do it on a membrane described previously [1]. Let us remember that the membrane in question is a cation-exchange membrane of sulfonated polyethylene.

Its capacity is 1.37 meq/g/sec, its inflation rate in 0.1M NaCl is 65%, and its thickness is 0.26 mm. In the presence of 0.1 M NaCl, we were able to measure

$$X = 2,139 \text{ moles/m}^3$$

$$K_E = 0.30 \text{ (international unit)}$$

$$h = 1.8 \cdot 10^{-2} \text{ m,}$$

and we find in the literature [17], for 0.1 M NaCl:

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$$t_1^0 = 0.385,$$

$$t_2^0 = 0.615,$$

$$D_s = 1.485 \cdot 10^{-9} \text{ m}^2/\text{s},$$

$$\alpha = 4.14 \cdot 10^{-5} \text{ m}^3/\text{equivalent},$$

$$\nu = 8.9 \cdot 10^{-7} \text{ m}^3/\text{s (at } 25^\circ\text{C)}$$

$$a = 0.595,$$

$$F = 96\,500,$$

$$g = 9.81 \text{ m/s}^2,$$

$$\bar{V}_0 = 1.8 \cdot 10^{-5} \text{ m}^3.$$

In the case of a very permselective membrane (t_1 near 1)

$$t_2 \approx \frac{V_1}{\bar{V}_0} - \frac{M_1}{M_0} = \frac{\bar{V}_1 - M_1}{18} \quad \text{with } \bar{V}_1 \text{ in cm}^3$$

Unfortunately, the partial molar volumes of the ions are not available for measurement; however, we can find an evaluation of them from

$$\bar{V}_i = \frac{4}{3} \pi r_i^3 N$$

where r_i = Stokes' radius and N = Avogadro's number.

From data in the literature [18] we calculated the values of t_{0s}/ρ varying from -1.25 to +1.78. Since t_{0s}/ρ remains small, by way of simplification we will say that it is near zero in the case of sodium chloride.

Coming back to expression (27), it is clear that we have to determine $\sigma_{(e)}$ in order to calculate $t_{0(app)}$; unfortunately, these values are not available to us.

We can nevertheless draw the following two conclusions:

-- the experiment shows that the water transport number is independent of the current density; and

-- the measured value of $t_{0(app)}$ is 12; in order to adjust the results of formula (27) with the experimental value, we must choose $\sigma_{(e)} = 0.66$, which is reasonable for this type membrane.²

We may thus estimate that there is good agreement between the experiment and theory. Fig. 3 sums up these conclusions.

However, we must not lose sight of all the approximations made for σ_e and t_{0s} . Further, the lack of experiments at other

² In order to conserve the same σ_e in the cases of the three profiles, we were led to choose $\bar{C}_2(e) = 139$, which is a little strong for this type of membrane (we measured 93), but still within reason.

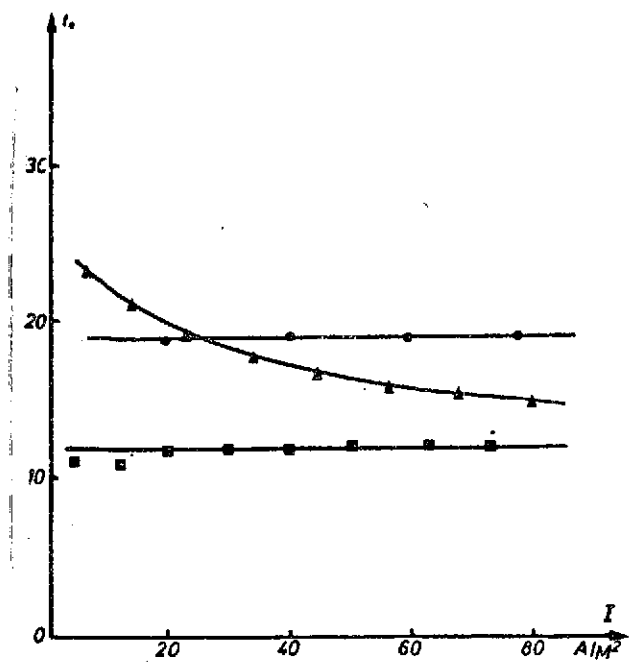


Fig. 3. Dependence of the apparent water transport number on current density.

Experimental points:

- Profile (a) under natural convection
- ▲ Profile (b) under natural convection.
- Profile (b) under imposed convection
- Curves calculated with equation (23)

concentrations and on other types of membranes limits for the moment the range of the result, which is still satisfactory.

Let us now proceed to the case of profile (b).

In this case, the term $G(I)$ is other than zero, since there is a gradient of chemical potential of the salt in the membrane. The use of relation (23) becomes very difficult.

Nevertheless, we can formulate simplifying hypotheses often encountered in the literature:

-- the diffusion coefficients are constant and equal to the equilibrium values;

-- the activity coefficient of the co-ion $\bar{\gamma}_2$ in the membrane is constant;

-- the electrochemical potential profile of the ions in the membrane is linear;

-- the saline solutions of compartments I and II behave ideally;

-- we will concede that the total exclusion of salt in the membrane varies little; and this is a good approximation for small disturbances

$$\begin{aligned} \langle \bar{C}_1 \rangle &\approx \bar{C}_1(\omega) \\ \langle \bar{C}_2 \rangle &\approx \bar{C}_2(\omega) \end{aligned}$$

-- finally, noting that in the expression of the electrochemical potential, the term

$$\bar{\mu}_2 + \bar{V}_2 P$$

varies little in the case of small disturbances, as a first approximation we can write:

$$\bar{D}_2 \int_{0+}^L \bar{C}_2(x) \frac{d\bar{\phi}}{dx} dx \approx \bar{D}_2 \bar{C}_2(\mu) \Delta \bar{\phi} \quad (31)$$

in which $\bar{\phi}$ is the electric potential and $\bar{C}_2(\mu)$ is the concentration already defined in (13).

It is clear that this group of hypotheses will be the more justified the less the system is disturbed by the electric field with regard to its equilibrium conditions. The behavior of $t_0(\text{app})$ which will be deduced from it must therefore be considered a behavior limit.

Under the above conditions, definition (18) of σ makes it possible for us to write:

$$\sigma \approx \sigma.$$

Let us return to the expression

$$\int_{0+}^L \bar{D}_2 \bar{C}_2 \frac{d\bar{\eta}_2}{dx} dx = \bar{D}_2(\mu) \bar{C}_2(\mu) \Delta \bar{\eta}_2 \approx \bar{D}_2(\omega) \bar{C}_2(\mu) \Delta \bar{\eta}_2$$

since we have assumed the diffusion coefficient to be constant.

Besides, according to the definition of the electrochemical potential, ignoring the pressure terms:

$$\frac{d\bar{\eta}_2}{dx} = RT \frac{d \ln \bar{C}_2}{dx} - F \frac{d\bar{\varphi}}{dx}$$

since $\bar{\gamma}_2$ is constant. Consequently:

$$\int_{0+}^{l-} \bar{D}_2 \bar{C}_2 \frac{d\bar{\eta}_2}{dx} dx = RT \bar{D}_{2(\omega)} \Delta \bar{C}_2 - \bar{D}_{2(\omega)} F \int_{0+}^{l-} \bar{C}_2 \frac{d\bar{\varphi}}{dx} dx$$

Taking into account (31), we have:

$$\bar{C}_2(\mu) [\Delta \bar{\eta}_2 + F \Delta \bar{\varphi}] = RT \Delta \bar{C}_2$$

or

$$\bar{C}_2(\mu) = \frac{\Delta \bar{C}_2}{\ln \frac{\bar{C}_2(\text{II})}{\bar{C}_2(\text{I})}}$$

in which $\bar{C}_2(\text{I})$ and $\bar{C}_2(\text{II})$ are the interfacial concentrations of co-ions (or exclusion salt) in the membrane. Finally, definition (16) becomes:

$$\bar{D}_2^* = \bar{D}_{2(\omega)} \frac{\Delta \bar{C}_2}{\bar{C}_{2(\omega)}} \cdot \frac{1}{\ln \frac{\bar{C}_2(\text{II})}{\bar{C}_2(\text{I})}}$$

If we express the concentration of the exclusion salt by the simplest relation, which is good for dilute solutions:

$$\bar{C}_2 = \frac{\Gamma}{X} (C_2)^2$$

where X is the capacity and Γ is the deviation coefficient with regard to Donnan's ideal excursion, then

$$\bar{D}_2^* = \bar{D}_{2(\omega)} \frac{2 \Delta C}{C \ln \frac{C(\text{II})}{C(\text{I})}} \quad (33)$$

in which $C = C^0(I) = C^0(II)$. This leads back to conceding that Donnan's equilibriums are not disturbed by the electric field. Since we assume the saline solution to be ideal, we have

$$\begin{aligned} \ln \frac{a_s(II)}{a_s(I)} &\simeq \ln \frac{C(II)}{C(I)} \\ G(I) &\simeq \frac{2\sigma_s F \bar{D}_s(\rho)}{\rho(1 + \sigma_s) \bar{V}_s C} \cdot \frac{\Delta C}{I} \end{aligned} \quad (34)$$

and, taking into account (30):

$$\begin{aligned} \Delta C &= \left(\frac{1}{K_D} \right)^{4/5} \cdot I^{4/5} \\ G(I) &\simeq \frac{2\sigma_s \bar{D}_s(\rho) F}{\rho(1 + \sigma_s) \bar{V}_s C (K_D)^{4/5}} \cdot \frac{1}{I^{1/5}} = \frac{k}{I^{1/5}} \end{aligned} \quad (35)$$

with k constant, independent of I , and, coming back to (26):

$$t_{0(app)} = \frac{t_{0s}}{\rho} + E(I) + \frac{k}{I^{1/5}}$$

We therefore anticipate that $t_{0(app)}$ in profile (b) must be a linear function of $I^{-1/5}$ of gradient k and the original ordinate $t_{0s}/\rho + E(I)$, $E(I)$ being in fact constant, as we have seen previously.

In the case of the preceding membrane $K_D = 0.335$ has been found [1], which leads from relation (25), taking our approximations into account, to

$$E(I) \simeq 0.$$

That is, $t_{0s}/\rho + E(I)$ remains quite close to zero; in the particular case of this membrane, the original ordinate of the straight line $t_{0(app)} = f(I^{-1/5})$ must be close to zero, but there is no a priori reason why this property would be general. As Fig. 4 shows experimentally [1], one can observe that $t_{0(app)}$ for profile (b) is a linear function of $I^{-1/5}$ of the original

ordinate close to zero. In order for the gradient calculated by relation (35) to be in good agreement with the measured gradient,

one is led to choose a value of $\bar{D}_2(e) = 6 \cdot 10^{-11}$ m²/sec, which is reasonable.

Considering the nature and the number of approximations made, we can regard this result as satisfactory.

2) Case of Imposed Convection

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In this case the phenomena are much more complex. However, in the case of agitations causing only a laminar flow of the fluid on the interfaces and with moderate polarization, it has been possible to show theoretically and experimentally [20, 21] that ΔC is proportional to I .

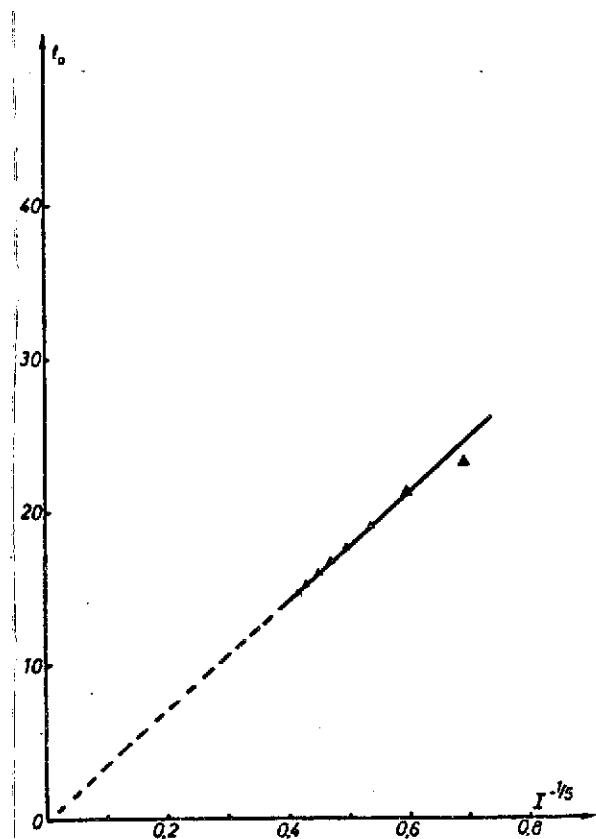


Fig. 4. Dependence of the apparent water transport number on $I^{-1/5}$. Case of profile (b) under natural convection.

Besides, if we impose such hydrodynamic conditions, that the thickness of the hydrodynamic layer could be considered constant at every point of the membrane, then the average thickness of the Nernst layer is also constant at first approximation [20].

Definition (25) shows that $E(I)$ does not depend on current density.

If we examine the case of profile (b) under imposed convection (experimental arrangement most often encountered in the literature), the above conditions permit the use of the limit formula (34), $t_0(\text{app})$ being naturally expressed by (26)

$$t_0(\text{app}) = \frac{t_{0s}}{\rho} + E(I) + G(I)$$

Since $\Delta C/I$ is independent of current density, so is $G(I)$.

In conclusion, $t_0(\text{app})$ must also be independent of current density. This result is confirmed by numerous researchers and on various cation- (14) and anion-exchange membranes.

Nevertheless, we must not close our eyes to the fact that this constancy of the transport number is generally still observed in the case of high polarizations and sometimes even beyond the critical current. The explanation for this phenomenon can obviously not be given by what has been presented. Further, certain researchers [12, 13, 14] have observed an increase in $t_0(\text{app})$ under agitation at very small current densities. We think that this phenomenon might be due to an intermediate convection between the natural convection and the imposed convection caused by the geometry of the cell and insufficient agitation. The consequence of this is an increase in $\Delta C/I$ and thus in $t_0(\text{app})$ at very small current densities.³

Let us finally note that in the case of profile (b), whether under natural or imposed convection, we obtained the following expression for $t_0(\text{app})$:

$$t_0(\text{app}) = A_1 + A_2 \frac{\Delta C}{I}$$

³ However, in the case of membranes highly permeable to the solvent this explanation is perhaps not sufficient (24).

in which A_1 and A_2 are different constants according to the type of convection.

As this expression is theoretically valid only for conditions close to equilibrium, we can compare it with the one obtained previously [1] through analysis according to the methods of the thermodynamics of irreversible processes, which has given an analogous result. This good accord between the two methods makes it possible to think that one can indeed ignore the couplings between the flows of the ions and of the water, at least in the particular case of this membrane [19].

In the case of the preceding membrane, in the presence of 0.1 M NaCl, we measured a relation $\Delta C/I = 0.5 \text{ A}^{-1}\text{m}^{-1} \text{ mole}$; when the thickness of the Nernst layer was chosen to be $\delta = 1.24 \cdot 10^{-5}$, and when the same values as previously were attributed to the other parameters of expression (26), the calculated value of $t_0(\text{app})$ coincides exactly with the measured value, which is 19.

An experimental evaluation of an average value of δ gave $1.2 \cdot 10^{-5} \text{ m}$.

Consequently, we may consider this agreement to be qualitatively satisfactory.

3) Case of Constant Thickness of the Nernst Layer

Let us consider the experimental arrangement sketched in Fig. 5. It is made up of a gel/ion-exchange membrane/gel sandwich separating two efficiently agitated electrolyte solutions. The gels are electrically and chemically inert and nonconvective. In them, the diffusion coefficient of the electrolyte is practically not affected with regard to its value in solution. For example, agarose gels meet such criteria [22]. Under these

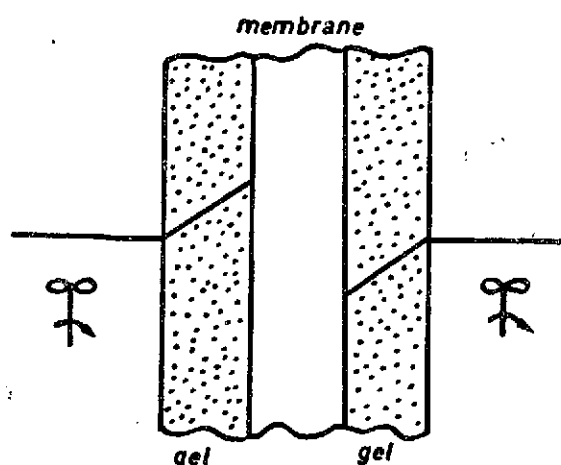


Fig. 5. Sketch of the experimental arrangement in which Nernst layers are constructed by means of gels.

conditions, the thickness of the Nernst layer is determined by the thickness of the gels, and is consequently constant. Then we may anticipate that ΔC will be proportional to I [23]. It is easy to see, according to the above, that the water transport number must be independent of current density. Measurements are being conducted at present in our laboratory to test this conjecture experimentally.

III. Conclusion

We may sum up the preceding considerations by presenting the influence of various factors on the water transport number. It is influenced by:

- a) parameters of the membrane: permselectivity of the membrane, intramembrane diffusion coefficients and degree of inflation;
- b) parameters connected with the type of electrolyte; ion transport numbers, diffusion coefficient, and concentration of the electrolyte;
- c) parameters of polarization characteristics of the membrane/electrolyte system: $\Delta C/I$ relation and the thickness of the Nernst layer; these quantities are highly dependent on the type of convection that exists on the membrane/solution interface;

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d) parameters outside the system: pressure and temperature.

We have shown that the dependence of the water transport number on current density is a function of $\Delta C/I$.

Since this quantity essentially depends on the type of convection existing on the surface of the membrane, we may conclude that the dependence of the water transport number on current density is a phenomenon connected with the hydrodynamic conditions of the system studied.

However, the lack of experimental results on various types of membranes does not allow us at present to consider this explanation theoretically.

In the experimental systems generally studied, the observed electroosmotic flow is a result of these various factors. In particular, the influence of polarization, as small as it may be, cannot be eliminated. That is why we think that rather than striving to do away with the influence of polarization, one should construct systems in which the hydrodynamic conditions and the interfacial concentration are well known; thus one will be able to bring forth, on various types of membranes, the relative influence of the parameters listed above. This is the direction in which we pursue our experimental investigations, particularly with the aid of gels.

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